

Smoothing of niobium by electropolishing

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Abstract The effects of various electropolishing (EP) parameters such as duration, applied voltage, working temperature, mechanical prepolishing and acid volume ratio on the EP process, and surface smoothness of high purity niobium (Nb) were systematically investigated using electrochemical technique and optical profilometry. The electropolishing parameters had a significant influence on the smoothness of the Nb by controlling the current density. Prolonged EP duration caused different dissolution rates of grains. Applied voltages above the oxygen evolution potential resulted in severe pitting of the Nb. High working temperature-caused roughening of the Nb surface via different dissolution rates of grains and mechanically ground smooth surfaces were roughened by the formation of valleys on the surfaces. A lower fluoride ion concentration in the acid solution gave rise to a rougher surface of the Nb because the fluoride ions were transport-limited species during the EP process.

Keywords Niobium · Electropolishing · Surface smoothness

1 Introduction

High purity niobium (Nb) is used to make superconducting radio frequency (SRF) cavities. SRF cavities are needed for particle acceleration in charged particle accelerators used for studying various aspects of high-energy physics, and SRF cavities are of increasing interest for these machines

[1]. The standard cavity fabrication process involves the formation of Nb half shells followed by electron beam welding to join them to form the cavity structure. Surface condition plays a critical role in the performance of SRF cavities, and so various routes for surface preparation have been developed [2, 3]. A typical SRF cavity preparation protocol includes buffered chemical polishing (BCP), performed using an acid mixture to remove the damaged surface layer, but this limits the performance of the cavities due to steps created at the grain boundaries [4–6]. Surface treatment has also been performed by centrifugal barrel polishing (CBP), which involves rotation of the cavities at high speed with abrasive media [3]. Electropolishing (EP) of SRF cavities in a solution with a 1:9 volume ratio of HF (48 %) to H₂SO₄ (96 %) has been widely used to achieve higher accelerating gradients by removing the damaged layer and providing a superior surface finish [1, 7].

EP is usually carried out in the current density plateau region of the electrochemical polarization curve [8] where dissolution occurs under mass transport control. The mass transport limiting species could be cations of a dissolving electrode (salt film mechanism), the acceptor ions that are anions from an electrolyte (acceptor mechanism), or the water molecules present in the electrolyte [9]. Studies of Nb EP by Tian et al. [10] and Eozenou et al. [11] indicated that the diffusion of fluoride ions to an electrode surface was the rate-controlling step. Elmore [12] studied the current (*i*)–voltage (*V*) relationship for copper EP in orthophosphoric acid system and attributed the polishing effect to a varying concentration gradient of dissolved metal ions over protrusions and valleys on a rough surface [12].

A recent study of Nb EP-measured potential transients during galvanostatic polarization and found potential jumps after a transition period that were consistent with

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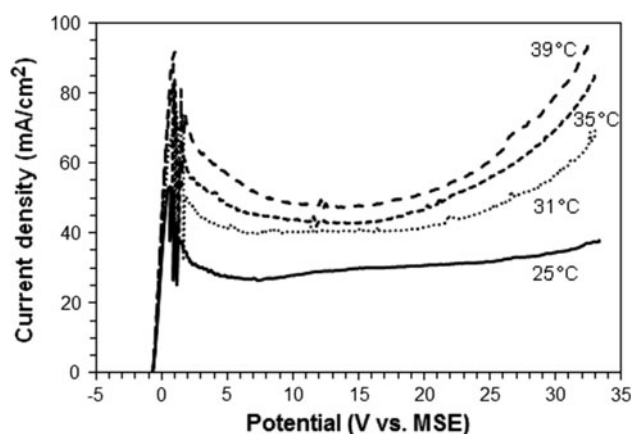


Fig. 1 Current densities of Nb, electropolished at different working temperatures and a HF:H₂SO₄ acid volume ratio of 1:9, as a function of potential

concentration polarization associated with the surface concentration of fluoride going to zero [7]. A simple model of fluoride transport through a surface layer matched the data. However, others have contended that a viscous surface layer is not required for EP [13].

The purpose of smoothening of Nb by EP for the application of SRF cavities is to improve the cavity performance by producing a better surface finish, which would result in higher accelerating gradients. Therefore, it is critical to understand the effects of various parameters on the *i*–*V* characteristics, EP rate, and surface smoothness of electropolished Nb. In this study, the effects of EP duration, applied voltage, working temperature, mechanical prep polishing, and acid volume ratio on the EP process and surface smoothness of high purity Nb were investigated using electrochemical techniques and optical profilometry. Mechanical prep polishing is used here as a means to study the effects of initial surface roughness.

2 Experimental details

Nb samples were saw cut from a 2.8-mm thick sheet of high purity (99.999 %) polycrystalline Nb, which is commonly used for making SRF cavities. The Nb samples were obtained from Fermi National Accelerator Laboratory, USA.

A schematic of the experimental setup and its detail descriptions were shown elsewhere [7]. The electrolytic cell was custom made of 99.999 % pure Al with inner dimensions of 23 × 4.8 × 5.2 cm³ because Al is passive and thus non-reactive in the HF-H₂SO₄ EP solution. The Al cell body was also used as the counter electrode in this

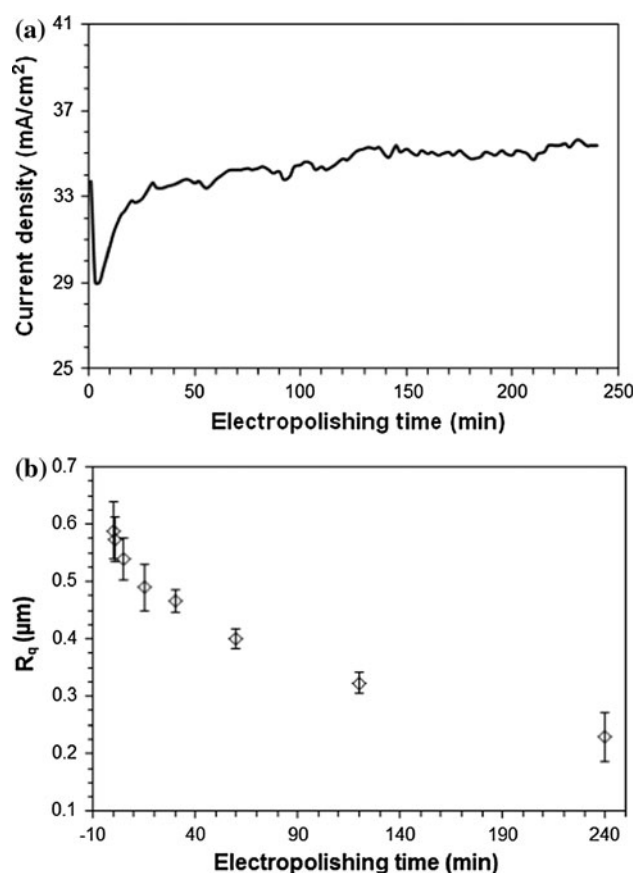
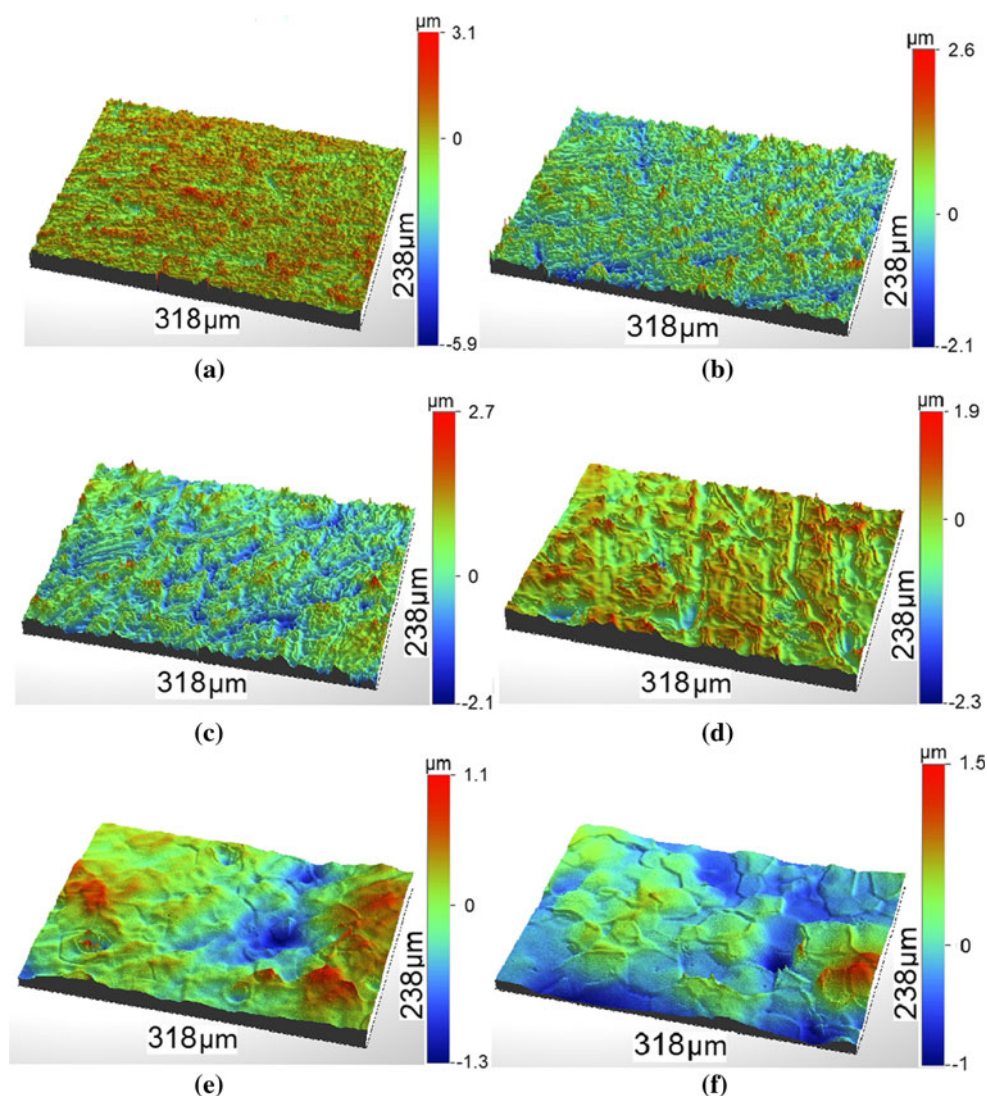


Fig. 2 **a** Current density of Nb, electropolished for 240 min at an applied voltage of 15 V, a working temperature of 25 °C and a HF:H₂SO₄ acid volume ratio of 1:9, as a function of EP time. **b** Root mean square (*R_q*) surface roughnesses of the Nb electropolished for different EP durations under the same conditions mentioned above

study. The working electrode was confined in a custom-built PTFE sample holder resulting in an exposed area of 1.32 cm². The reference electrode used for measuring the surface potential was mercury-mercurous sulfate (MSE) reference electrode with a potential of +0.64 V vs. SHE. The MSE reference electrode was used to prevent the problem of chloride contamination associated with the saturated calomel (SCE) reference electrode. The electrolyte was a 1:9 volume mixture of HF (48 %, Mallinckrodt Chemicals) and H₂SO₄ (96.2 %, Fisher Scientific).

A voltage was applied between the Nb working electrode and Al counter electrode by a computer controlled power supply (Sorensen XDL 35-5P), which also measured the current. A Fluke 8845A digital multimeter, which could be interfaced to a computer, simultaneously measured the potential between the Nb working electrode and the MSE reference electrode. The data acquisition was supported by

Fig. 3 Surface topographies of Nb electropolished for different EP durations: **a** 0, **b** 15, **c** 30, **d** 60, **e** 120, **f** 240 min, at an applied voltage of 15 V, a working temperature of 25 °C and a HF:H₂SO₄ acid volume ratio of 1:9



a customized LabVIEW program. The polarization i - V curves were measured by scanning the voltage between the working electrode and the counter electrode at a rate of 0.1 V/s from 0 to 35 V. The polarization curves were plotted as measured current as a function of measured potential versus the MSE reference electrode. Constant voltage measurements were made at a constant cell voltage between the reference and counter electrodes.

The temperature of the electrolyte was maintained within ± 0.5 °C of the intended value by placing the Al cell in a water bath. The temperature of the electrolyte was monitored using a thermocouple inserted near the sample.

The surface finish after EP was characterized using optical profilometry (OP, Contour GT K1 OP from Veeco). The supporting software (Vision 64) provided root mean square surface roughness (R_q), which was used for com-

paring the surface finish obtained under different conditions. The OP scanned an area of 318 by 238 μm at a magnification of 20 \times .

3 Results and discussion

Figure 1 shows the typical polarization curves of Nb EP in a standard acidic solution with a HF:H₂SO₄ acid volume ratio of 1:9 at different working temperatures. It is important to understand that the cell voltage was scanned while the current and electrode potential were measured so that the potential is not strictly the independent variable. The form of these polarization curves is similar to that observed previously [7]. Four major regions can be identified with increasing potential: etching region at low

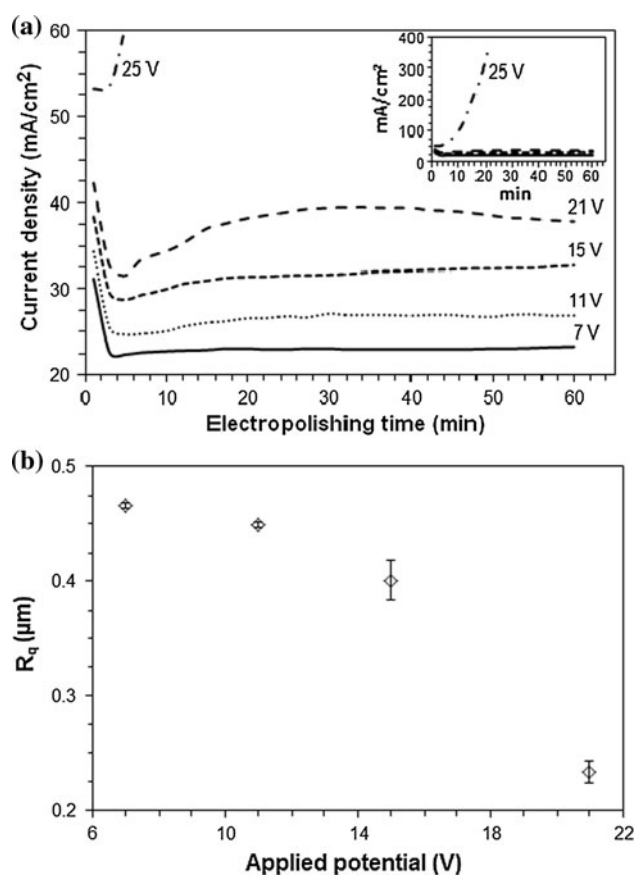
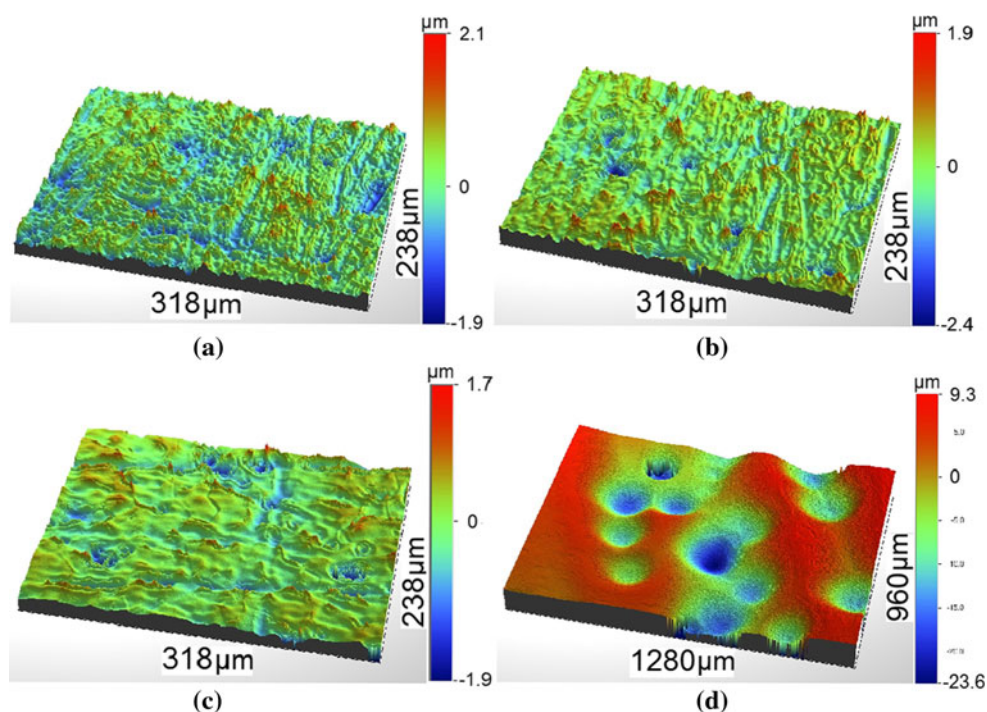


Fig. 4 **a** Current densities of Nb, electropolished for 60 min at different applied voltages, a working temperature of 25 °C and a HF:H₂SO₄ acid volume ratio of 1:9, as a function of EP time. **b** Root-mean-square (R_q) surface roughnesses of the Nb electropolished at different applied potentials under the same conditions mentioned above

Fig. 5 Surface topographies of Nb electropolished for 60 min at different applied voltages: **a** 7, **b** 11, **c** 21, and **d** 25 V, a working temperature of 25 °C and a HF:H₂SO₄ acid volume ratio of 1:9



potentials, oscillation region, polishing region with relatively constant current and gas evolution region at high potentials. The current density increases exponentially with increasing potential in the etching region due to activation polarization caused by crystallographic etching. The current density reaches a peak value and exhibits oscillations and then stabilizes at a plateau value that is relatively constant over a wide range of potentials. For EP systems following the acceptor mechanism such as Nb, the current fluctuations are likely associated with the formation of a viscous layer close to the electrode surface that balances the increased rate of reaction at higher potential [7, 14]. The best EP conditions are found in the current density plateau region [7]. The sharply increased current density beyond the current density plateau is a result of oxygen evolution on metal surface along with metal dissolution. EP in this potential region results in a rougher surface because of the disrupting effects of oxygen bubbles.

Figure 1 shows that the current density of the Nb significantly increases with increased working temperature throughout the entire potential range because of higher diffusivity of the electrochemically active species (e.g., F^-) in the electrolyte which in turn accelerates the reaction rate of the Nb [7, 10]. The larger value of plateau current density indicates that the Nb EP rate in this region increases with increased working temperature. However, the current density plateau becomes narrower with higher working temperature because of earlier oxygen evolution associated with the accelerated oxygen evolution process. Therefore, the lowest temperature

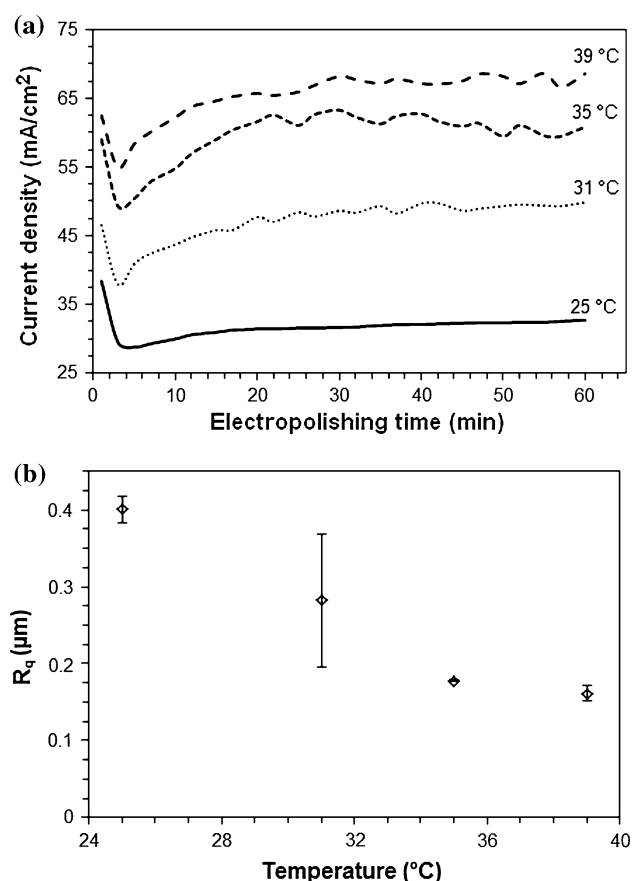


Fig. 6 **a** Current densities of Nb, electropolished for 60 min at an applied voltage of 15 V, different working temperatures and a HF:H₂SO₄ acid volume ratio of 1:9, as a function of EP time. **b** Root mean square (R_q) surface roughnesses of the Nb electropolished at different working temperatures under the same conditions mentioned above

studied, 25 °C, exhibits the widest current density plateau. The working temperature of 25 °C together with an applied voltage of 15 V, which is below the potential at which the oxygen evolution starts, were selected as standard EP parameters for further characterization and comparison.

Figure 2a shows a representative plot of the current density during about 4 h of EP at an applied voltage of 15 V, a working temperature of 25 °C and a HF:H₂SO₄ acid volume ratio of 1:9. The current density first decreases probably owing to oxide film formation and goes through a minimum and then increases when the film breaks down [15].

Figure 2b shows the R_q values of the samples investigated after different EP durations. The R_q value of the Nb mechanically ground using 320 grit SiC paper is about 0.59 μm. The EP of the Nb for 1 and 5 min results in the R_q values of about 0.57 and 0.54 μm, respectively. The small

changes indicate that EP for 5 min results in little improvement of the surface finish of the mechanically ground Nb. However, the R_q value of the Nb significantly decreases from about 0.49 to 0.23 μm when the EP duration is increased from 15 to 240 min. It is clear that the longer EP duration gives rise to smoothening of the Nb surface.

Figure 3 shows the surface topographical maps from the optical profilometry of the Nb electropolished for different EP durations. Different samples were used for experiments with different EP durations. It is important to notice the ranges of the false color scale bars to the right of each image to appreciate the changes in roughness. Dense protruding asperities above the surface of the mechanically ground Nb using 320 grit SiC paper are apparent in Fig. 3a. EP for 15 min reduces the roughness because of leveling of the surface asperities as expected for an EP process, Fig. 3b. This effect can be more clearly seen for the longer EP of about 30 min as shown in Fig. 3c. After 60 min, the protruded surface asperities on the Nb are almost level as seen in Fig. 3d. Prolonged EP for about 120 min results in a change in the lateral dimension of the roughness, causing a waviness of the surface, Fig. 3e. Eventually, the roughness of the surface is controlled by variation in the dissolution of grains, but the roughness is extremely low after EP for 240 min as shown in Fig. 3f. Differing dissolution rates of grains with different crystallographic orientation seem to limit the ultimate smoothness achievable by EP.

The effect of applied voltage on topography was studied at a working temperature of 25 °C because the widest current density plateau was exhibited at this temperature in Fig. 1. Figure 4a shows the curves of current density versus time of the Nb electropolished at different applied voltages, a working temperature of 25 °C and a HF:H₂SO₄ acid volume ratio of 1:9 for about 60 min. At 25 V, the current density increases dramatically after a few min because of oxygen evolution on the metal surface with significant metal dissolution [9]. Therefore, the applied voltage of 25 V is clearly not suitable for Nb EP. At lower applied voltages, the current density first decreases and goes through a minimum related to the formation and stabilization of the viscous layer [15]. Typical surface topographical maps of the Nb surfaces after about 60 min of EP at different applied voltages are shown in Fig. 5 and the R_q values for each voltage are given in Fig. 4b. Note that the topography of the surface after EP at 15 V for 60 min was shown in Fig. 3c.

Comparison of the topographic images of the EP samples in Fig. 5 with the as-prepared sample, Fig. 3a, shows that the EP process smoothenes the surfaces for all applied voltages except for 25 V. This decrease in

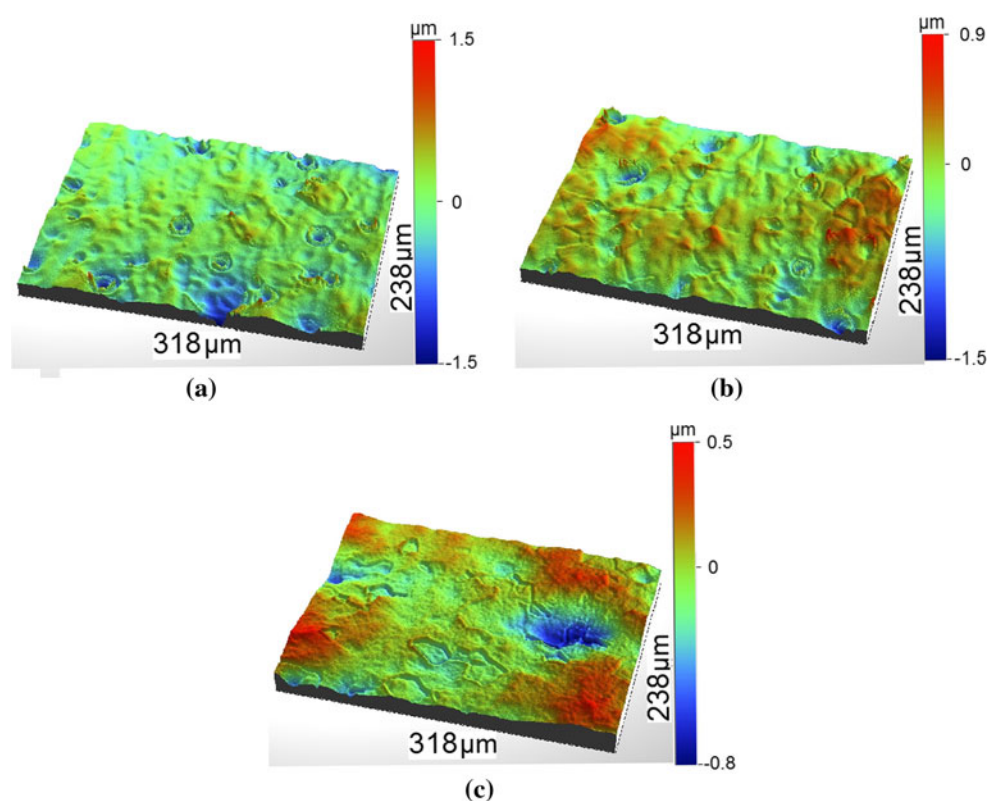


Fig. 7 Surface topographies of Nb electropolished for 60 min at an applied voltage of 15 V, different working temperatures: **a** 31, **b** 35, and **c** 39 °C and a HF:H₂SO₄ acid volume ratio of 1:9

roughness is also evident in Fig. 4b where R_q is seen to decrease with increasing applied voltage. The smoothest surface is found after EP at 21 V. However, as shown in Fig. 4a, the current is much larger at this voltage, so the charge passed during the 60 min treatment was greater, which might have accounted for the improved smoothness of the surface. The extreme roughness created at the highest voltage of 25 V is evident in Fig. 5d and the large surface features suggest a strong effect of oxygen bubbles, which were observed on the surface. Occluded regions caused by the presence of the bubbles result in localized attack that is very deep compared to the other surface features [15].

The effect of temperature over the range of 25–39 °C was also studied. The current densities of the Nb electropolished for about 60 min at different working temperatures are presented in Fig. 6a. The form of the curves is generally the same at all temperatures. However, the current density increases with increased working temperature during the entire polishing time probably due to the enhanced diffusivity of species (e.g., F^-) in the electrolyte [7, 10]. Fluc-

tuations in current density observed at higher temperatures probably result from variations in local temperature associated with insufficient temperature control.

Typical surface topographical maps of the Nb surfaces after about 60 min of EP at 15 V and different temperatures are shown in Fig. 7 and the R_q values for the different temperatures are given in Fig. 6b. Note that the topography of the surface after EP at 25 °C was shown in Fig. 3c. Much like what was found with increasing potential, roughness decreases as the EP temperature increases. The roughness decreases steadily as the temperature increases from 25 to about 35 °C but little further improvement was found by increasing the temperature to 39 °C. The overall roughness at 39 °C was low but further improvement was limited by localized attack as well as grain etching. The improvement in roughness with temperature again scales with the increasing current and thus charge measured with increasing temperature.

The effect of mechanical pre-abrasion on the EP of Nb was investigated by grinding the Nb using different grit SiC paper to get different surface roughness. Figure 8a

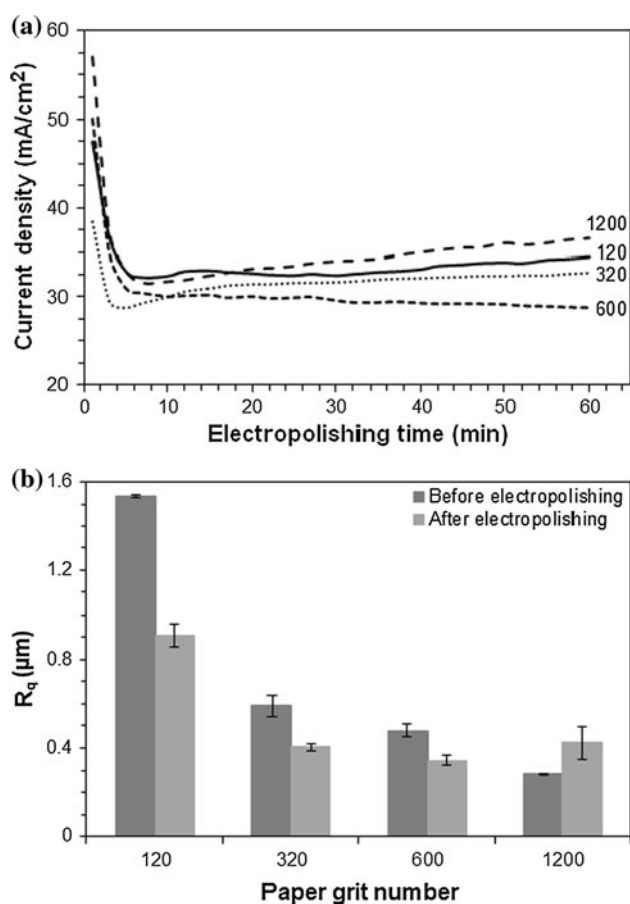


Fig. 8 **a** Current densities of Nb, mechanically pre-polished using different grit SiC papers and electropolished for 60 min at an applied voltage of 15 V, a working temperature of 25 °C and a HF:H₂SO₄ acid volume ratio of 1:9, as a function of EP time. **b** Root mean square (R_q) surface roughnesses of the Nb measured before and after EP under the same conditions mentioned above

presents current traces of the Nb with the different pre-treatments for EP at 15 V and 25 °C. Typical surface topographical maps of the Nb surfaces after mechanical pre-abrasion and then after EP are shown in Fig. 9 and the R_q values for the different pre-treatments are given in Fig. 8b. The current density traces of the samples with different pre-treatments are similar. In this case, the improvement in roughness does not scale with the current density and charge. The roughness of the as-abraded surfaces decreases with increasing paper grit number as expected. The improvement in roughness with EP is best for the sample abraded with 120 grit paper. Samples abraded with 320 and 600 grit papers behave similarly, though the R_q value after abrasion is slightly smaller for the 600 grit sample. The current density for the sample abraded with 1,200 grit SiC paper is the largest and exhibits the

steepest increase with EP time. The roughness actually increases as a result of EP for the 1,200 grit sample. Figure 9e, f shows that surface dimpling during EP is responsible for the greater roughness.

The influence of increasing HF:H₂SO₄ acid volume ratio over the range of 1:9 to 0.1:9.9 was also studied. The 1:9 volume ratio of HF:H₂SO₄ was used as a standard electrolyte in this study. Figure 10 shows the polarization curves for different acid volume ratios. The current density over the wide range of applied potentials decreases with decreased content of HF in the solution. This supports the notion that Nb EP follows the acceptor ion mechanism with fluoride ion being the transport limited species [7, 10, 11]. Nb normally has a thin stable oxide layer of Nb₂O_{5-x} but this passive layer is unstable in the presence of fluoride ions. HF is therefore indispensable for Nb EP. It is clear that the decreased fluoride ion concentration associated with decreased fraction of HF in the solution is responsible for the decreased current density during the EP because the fluoride ions are the rate controlling species [7, 10, 11, 14].

The current density traces measured during EP at 15 V follow the same trends as the polarization curves, as shown in Fig. 11a. In addition, the decrease in current density that is clearly seen for the early stages of EP in the solution with HF:H₂SO₄ acid volume ratio of 1:9 becomes much less evident as the ratio decreases. The HF feed was only 48 % acid so larger concentrations of HF result in higher water content in the solution. This actually improves oxide stability because the oxide film can easily form on the Nb surface in the aqueous solution [16, 17]. Though the solution with the highest fraction of HF has the highest concentration of fluoride ions, the charge still passed in the initial stage clearly confirms the fast and easy formation of the oxide film on the Nb surface in the aqueous solution.

Typical surface topographical maps of the Nb surfaces after about 60 min of EP at 15 V and 25 °C but different acid ratios are shown in Fig. 12 and the R_q values for the different acid ratios are given in Fig. 11b. Note that the topography of the surface for the standard acid ratio of 1:9 was shown in Fig. 3c. The R_q value of the electropolished Nb increases from about 0.4 to 0.55 μm with decreased fraction of HF in the solution from 1 to 0.1, as shown in Fig. 11b, so the R_q value of the electropolished Nb at the HF:H₂SO₄ acid volume ratio of 0.1:9.9 for about 60 min is only slightly smaller than that (0.59 μm) of the mechanically pre-polished Nb using 320 grit SiC paper. Therefore, the highest density of the surface asperities is found on the electropolished Nb at the lowest

Fig. 9 Surface topographies of Nb, mechanically pre-polished using **a, b** 120, **c, d** 600, and **e, f** 1,200 grit SiC papers, measured **a, c, e** before and **b, d, f** after EP for 60 min at an applied voltage of 15 V, a working temperature of 25 °C and a HF:H₂SO₄ acid volume ratio of 1:9

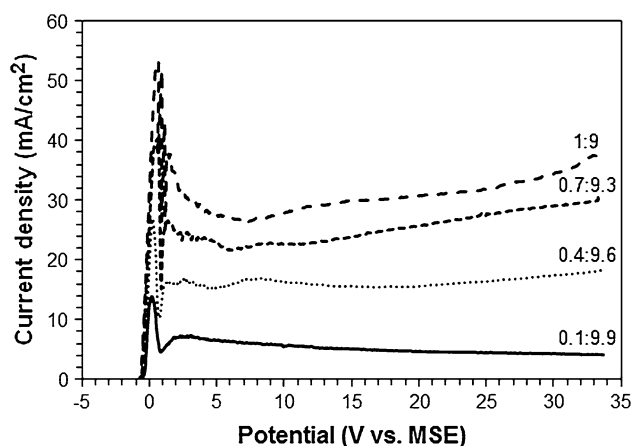
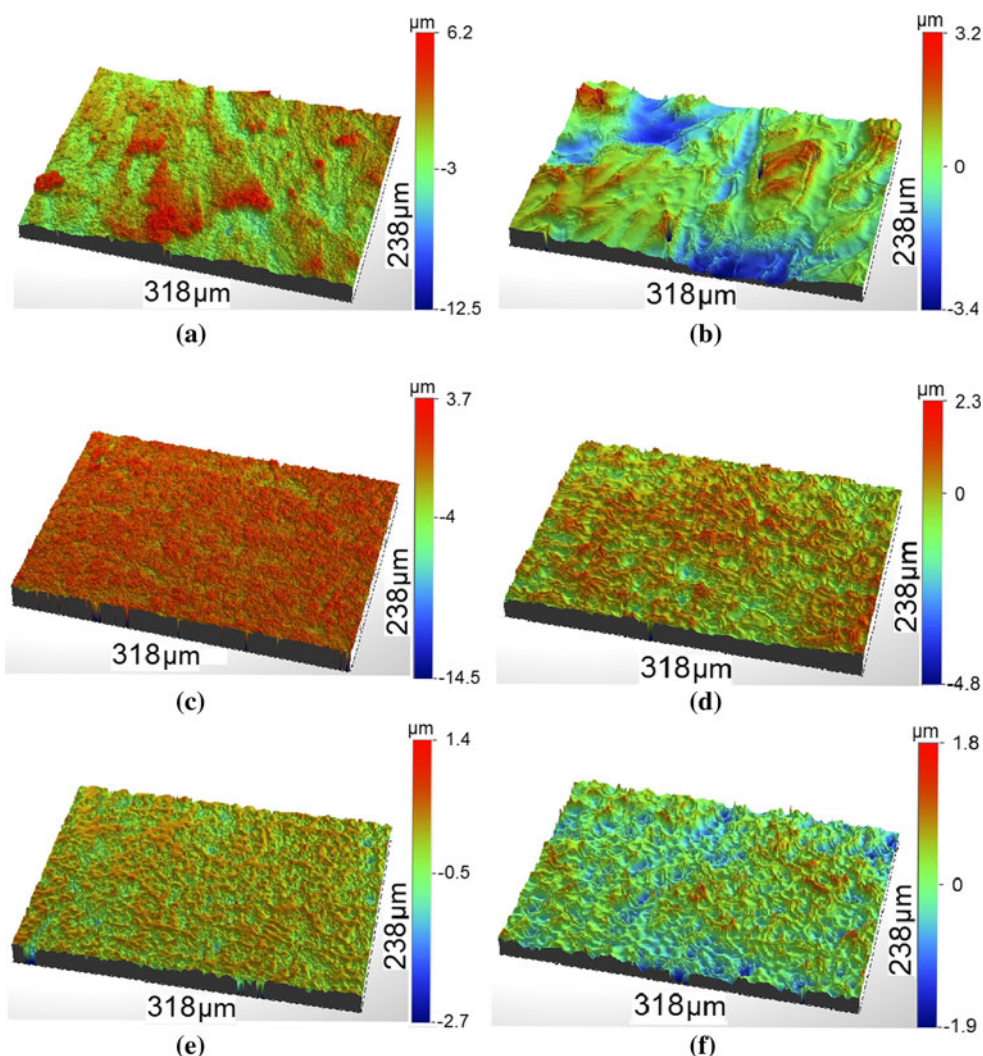


Fig. 10 Current densities of Nb, electropolished at a working temperature of 25 °C and different HF:H₂SO₄ acid volume ratios, as a function of potential

fraction of HF in the solution for 60 min as shown in Fig. 12.

4 Conclusions

The effects of EP duration, applied voltage, working temperature, mechanical pre-polishing and acid volume ratio on the EP of Nb were investigated. The following can be concluded:

1. Increased EP duration smoothened the surface of the Nb via the preferential dissolution of the surface asperities, although the prolonged EP resulted in the different dissolution rates of grains having different crystallographic planes.

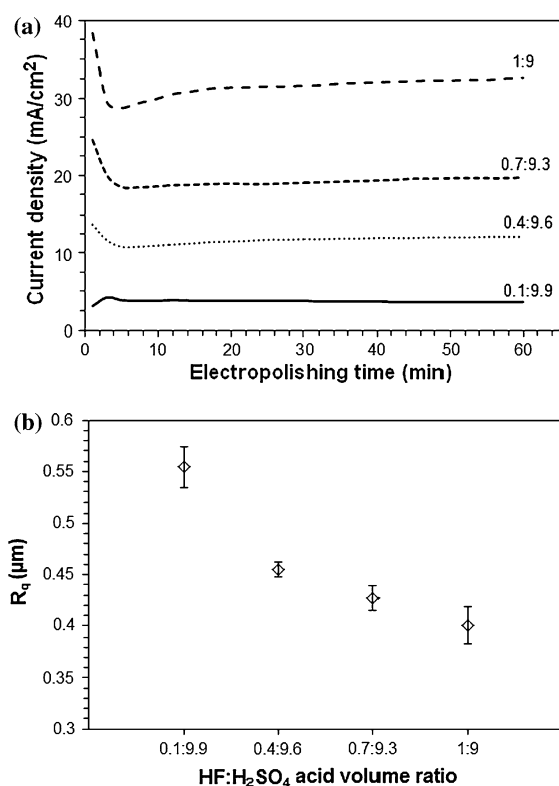
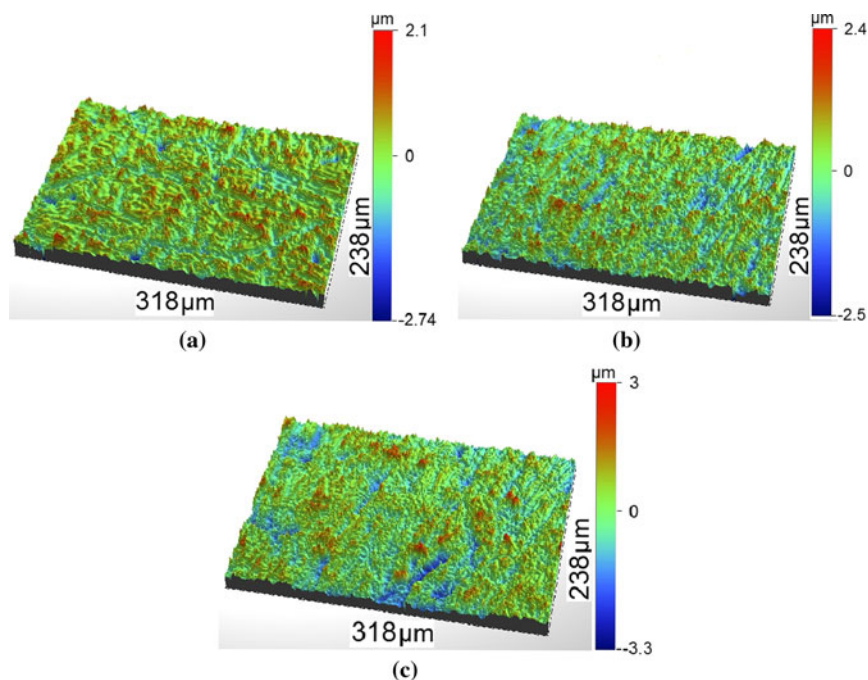


Fig. 11 **a** Current densities of Nb, electropolished for 60 min at an applied voltage of 15 V, a working temperature of 25 °C and different HF:H₂SO₄ acid volume ratios, as a function of EP time. **b** Root mean square (R_q) surface roughnesses of the Nb electropolished at different HF:H₂SO₄ acid volume ratios under the same conditions mentioned above

2. Increased applied voltage significantly reduced the surface roughness of the Nb during the same EP duration. However, at an applied voltage higher than the oxygen evolution potential resulted in the severe pitting of the Nb surface.
3. The surface of the Nb became smoother with higher working temperature due to the promoted diffusivity of electrochemically active species (e.g., F⁻) in the electrolyte. EP of at 39 °C produced the smoothest surface finish as further improvement was limited by localized attack as well as grain etching.
4. When the fraction of HF in the HF:H₂SO₄ acid solution was decreased, the reduced fluoride ion concentration degraded the effective EP of the Nb so the roughest surface topography of the Nb was found at the smallest fraction of HF in the solution.
5. The initial surface roughness of the mechanically ground Nb had a significant effect on its EP so the rougher surface of the ground Nb had the faster EP rate. The EP of the ground Nb with the relatively smooth surface, however, produced a rougher surface by forming valleys on the surface.
6. The best surface finish of Nb can be obtained by EP of the mechanically ground Nb using 320 grit paper for about 240 min at an applied voltage of 15 V, a working temperature of 25 °C and a HF:H₂SO₄ acid volume ratio of 1:9.

Fig. 12 Surface topographies of Nb electropolished for 60 min at an applied voltage of 15 V, a working temperature of 25 °C and different HF:H₂SO₄ acid volume ratios: **a** 0.7:9.3, **b** 0.4:9.6, and **c** 0.1:9.9



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References

1. Padamsee H, Knobloch J, Hays T (2008) RF Superconductivity for accelerators. 2nd edn. Wiley-VCH, New York
2. Shemelin V, Padamsee H (2008) Magnetic field enhancement at pits and bumps on the surface of superconducting cavities, TTC-Report 2008-07
3. Higuchi T, Saito K, Noguchi S, Ono M, Kako E, Shishido T, Funahashi Y, Inoue H, Suzuki T (1995) Proceedings of the 1995 workshop on RF superconductivity, Gif-sur-Yvette, France, pp 723–727
4. Padamsee H (2009) RF superconductivity: science, technology and applications, Wiley-VCH, Weinheim
5. Palmieri V, Stivanello F, Stark SY, Roncolato C, Valentino M (2001) Besides the standard niobium bath chemical polishing. 10th Workshop on RF superconductivity, Tsukuba
6. Saito K, Inoue H, Kako E, Fujino T, Noguchi S, Ono M, Shishido T (1998) Superiority of electropolishing over chemical polishing on high gradients. Part Accel 60:193
7. Chandra A, Sumption M, Frankel GS (2012) On the mechanism of niobium electropolishing. J Electrochem Soc 159:C485
8. Jacquet PA (1935) Electrolytic method for obtaining bright copper surfaces. Nature 135:1076
9. Landolt D (1987) Fundamental aspects of electropolishing. Electrochim Acta 32:1
10. Tian H, Corcoran SG, Reece CE, Kelley MJ (2008) The mechanism of electropolishing of niobium in hydrofluoric–sulfuric acid electrolyte. J Electrochem Soc 155:D563
11. Eozenou F, Aspart A, Antoine C, Malki B (2006) Electropolishing of niobium: best EP parameters. CARE-Report-06-010-SRF. EU contract number RII3-CT-2003-506395
12. Elmore WC (1939) Electrolytic polishing. J Appl Phys 10:724
13. Rokicki R, Hryniewicz T (2012) Enhanced oxidation-dissolution theory of electropolishing. Trans Inst Met Finish 90:188
14. Palmieri V (2003) Fundamentals of electrochemistry: the electrolytic polishing of metals: application to copper and niobium. 11th Workshop on RF superconductivity, Germany
15. Landolt D, Chauvy PF, Zinger O (2003) Electrochemical micromachining, polishing and surface structuring of metals: fundamental aspects and new developments. Electrochim Acta 48:3185
16. Ricker RE, Myneni GR (2010) Evaluation of the propensity of niobium to absorb hydrogen during fabrication of superconducting radio frequency cavities for particle accelerators. J Res Natl Stand Technol 115:353
17. Halbritter J (1987) On the oxidation and on the superconductivity of niobium. Appl Phys A 43:1